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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: **PROCESS FOR THE PREPARATION OF CELLULOSIC FIBRE-REINFORCED THERMOPLASTIC COMPOSITE MATERIALS**

**(57) Abstract**

A process for the preparation of a composite material containing a thermoplastic polymer and cellulosic fibres, having high tensile and flexural properties, reduced thermal expansion and high thermal stability (heat-deflection temperature), compared to the pure plastic is described. Cellulosic fibres are coated with electron beam-curable monomers, oligomers or mixtures thereof. The coated fibres are mixed with a powdered thermoplastic matrix material. The mixture is electron beam treated to a specified dose, to chemically cure the fibre coating by producing free radicals in the fibre, in the coating and in the matrix polymer. Free radical reactions form chemical bonds between the fibres and the synthetic matrix. Mechanical bonding, the result of a molecular entanglement, further improves the adhesion between the wood fibres and the thermoplastic polymer.

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PROCESS FOR THE PREPARATION OF CELLULOUSIC FIBRE-  
REINFORCED THERMOPLASTIC COMPOSITE MATERIALS

This invention relates to a process for the  
5 preparation of a composite material containing a  
thermoplastic polymer and cellulose fibres, having high  
tensile and flexural properties, reduced thermal  
expansion and high thermal stability, when compared to  
pure plastics. More specifically, this invention  
10 relates to a process for the preparation of a composite  
material containing a thermoplastic polymer, cellulosic  
fibres, and electron beam-curable coupling agents,  
wherein the components of the composite material are  
treated with electron beam radiation before or after  
15 compounding to produce free radicals resulting in the  
formation of chemical bonds between the fibres and the  
synthetic matrix.

Background and Prior Art

Wood fibres and wood flour are currently used  
20 industrially as filler materials for various  
thermoplastics such as polypropylene, polyethylene, nylon  
and polyesters to produce blends with high elastic  
moduli, higher stiffness, reduced heat sensitivity and  
lower overall production costs, including both material  
25 and energy cost for processing. The adhesion between the  
fibres and the matrix significantly affects many of the  
properties of the composites. Chemical bonding between  
the hydrophilic wood fibres and the hydrophobic polymer  
cannot be achieved with standard mixing procedures.  
30 Therefore, the produced composite has reduced tensile,  
impact and flexural strength and increased moisture  
absorption, as compared to the pure polymer.

Several methods have been suggested and studied  
for improving the adhesion between wood fibres and  
35 thermoplastic matrices.

The fibres can be coated with mixtures of  
monomers, such as styrene and chemical initiators, such  
as benzoyl peroxide. The coating is polymerized and

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bonding occurs during mixing at an elevated temperature, or during extrusion. Molecules of the polymerized coating become intertwined with the polymer molecules, during processing, producing a mechanical bond.

5 U.S. Patent 4,464,510 discloses a method of producing a composite system consisting of thermoplastics and a natural fibre bonded with an unsaturated polyester resin without the addition of an initiator. As an optional step, this patent teaches that chemical  
10 initiators or radiation can be used. When radiation is used, it is disclosed that the wood fibres are pretreated with ionizing radiation before admixing with the unsaturated polyester resin. The present invention is a significant improvement over this prior art patent in  
15 specifying more efficient chemically reactive coupling agents and in elaborating a more technically feasible method for radiation processing. Specifically, in the process of the present invention, irradiation occurs after the fibres have been coated with an electron beam-  
20 curable coupling agent and mixed with the thermoplastic polymer. The wood fibre-filled thermoplastic polymers thus produced have improved mechanical properties over the prior art products.

U.S. Patent 3,645,939 describes mixing  
25 ethylenically unsaturated carboxylic acid or anhydride coupling agent, thermoplastic materials containing labile atoms, a hydroxy group containing material, such as cellulose, and treating with a free radical generating catalyst, including ionizing radiation. Such a system  
30 forms a bridge between the matrix and the hydroxy group containing material.

U.S. Patent 4,380,522 discloses a process for the manufacture of shaped articles from polyolefine compositions, modified by means of polar monomers, and  
35 cellulosic fibres. The polar monomers of this reference-

include unsaturated monocarboxylic acids such as acrylic, methacrylic or chloroacrylic acid, or unsaturated polycarboxylic acids such as maleic, fumaric and itaconic acid, or the anhydrides derived from these acids, such as maleic anhydride. The polyolefine and polar monomers are graft polymerized by either irradiation or in the presence of initiators. The modified polyolefine or unmodified polyolefine and polar monomers are mixed with the cellulose and subjected to a malaxating operation at high temperature.

Each of the suggested methods for improving the adhesion between wood fibres and thermoplastic matrices, has seen limited success and industrial acceptance. Select coupling agents have been shown to improve the mechanical properties of some specific matrix/fibre composites but the agents cannot be used universally. The ability of a specific chemical to couple a polymer and a fibre, depends on the polymer type, the wood species and the wood composition (bleached or unbleached). Coupling agents must be tailored to each specific wood fibre - reinforced composite, often making their industrial use impractical.

Coating the wood fibres with a polymer, such as polystyrene, prior to compounding, provides a surface for the matrix to bond through molecular entanglement, but does not provide a chemical bond between the coating and the fibre. Initiating polymerization of the coating by introducing chemicals such as benzyl peroxide, along with mixing/compounding at elevated temperatures, may also cause the fibres to clump together, lowering the final mechanical properties of the composite because of poor fibre dispersion.

Irradiating wood fibres in air produces peroxides and hydroperoxides on the surface of the fibres. Their concentration and distribution on the surface depends on

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the wood species, the wood composition (bleached or unbleached), the dose, the dose rate, the temperature during irradiation and the availability of oxygen to the fibres. The number of these active peroxide sites  
5 available to initiate polymerization of a coating, may also be a function of the time between the fibre irradiation and the application of the coating. Such complexities make the optimization of this method and the production of a consistent product difficult.

10 The use of ethylenically unsaturated carboxylic acid or anhydride along with a free radical catalyst can only be used with hydroxy group containing materials, producing weak hydrogen bonds between the matrix and the fibres and limiting the reinforcing benefits.

15 Therefore there is a need for a process to produce fibre-reinforced plastic composites with good mechanical and thermal properties which overcome the disadvantages of the prior art processes. The thermoplastic composite material of the present invention, contain chemical bonds  
20 between the fibre/coupling agent interface and the coupling agent/thermoplastic polymer.

#### Summary of the Invention

The process of the present invention is based on  
25 the recognition that a fibre-reinforced plastic composite with good mechanical and thermal properties can be formed if a chemical bond between the plastic matrix and the fibre's natural polymer is ensured by using EB-curable unsaturated oligomers, vinyl monomers, acrylate monomers, or their mixtures as coupling agents and treating the components of the composite with an electron beam after mixing the treated fibre with the thermoplastic material. Upon electron beam treatment, these reactive additives can form an adhesion-mediated  
30 layer of the fibre matrix interface.  
35

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In the process of the present invention, the wood fibres are coated with an electron beam (EB)-curable monomer/oligomer mixture. The coated fibres are then mixed with a powdered thermoplastic matrix material. The 5 mixture is EB treated to a specific dose prior to or after extrusion or other similar procedures resulting in intimate melt-mixing, to chemically cure the fibre coating by producing free radicals on the fibre surfaces, in the coating and in the matrix polymer. Free radical reactions during further compounding and extrusion will 10 form chemical bonds at both the coating/fibre interface and the matrix/coating interface. Mechanical bonding, the result of a molecular entanglement at the matrix/coating interface further improves the adhesion 15 between the wood fibres and the thermoplastic polymer.

In one embodiment of the present invention there is provided a process for the preparation of a thermoplastic material containing thermoplastic polymer, cellulose fibre and EB-curable coupling agents comprising 20 the steps of: treating the fibres 10 to 50% by weight of the total composite, with a coupling agent mixture in an amount of 1 to 10% by weight, related to the fibre; mixing the treated fibres with a thermoplastic powder, 45 to 90% by weight of the total composite and electron 25 beam treating the mixture to a dose of 5 to 50 kGy to produce free radicals; and compounding the cured mixture to form chemical bonds at the fibre-resin interface and the resin-polymer interface.

30 Detailed Description

In preparing the thermoplastic composite materials of the present invention, 45 to 90% by weight, preferably 55 to 75% by weight, of the thermoplastic polymer and 10 to 50% by weight, preferably 20 to 35% by 35 weight, of a cellulosic fibr are us d. The fibres are

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treated with an EB-curable coupling agent consisting of unsaturated polyesters and/or vinyl monomers and/or acrylated monomers/oligomers in an amount of 1 to 10% by weight, preferably 1.5 to 7% by weight, related to the  
5 fibre mass. The fibres are mixed with thermoplastic powder (melt flow index greater than or equal to 5 gram/10 minutes) and the mixture is electron beam treated to a dose of 5 to 50 kGy, preferably 6 to 16 kGy, prior to standard thermoplastic processing such as extrusion,  
10 injection moulding, calendering or thermoforming.

Examples of cellulosic material which can be used in the present process include seed fibres such as cotton, woody fibres such as coniferous and deciduous woods, bast fibres represented by flax, leaf fibres such  
15 as sisal, and fruit fibres such as coconut. However, wood fibres are preferred.

Various thermoplastic materials can be used in the present invention. For example, materials such as polypropylene, polyethylene, and polyvinyl chloride.  
20 These polymers are preferred, however, other thermoplastics such as copolymers of olefines, styrenes, acrylics, as well as polycarbonates, polyamides and polyesters could also be used in the present invention.

The properties of wood fibre-filled polyester polymers can be significantly improved if the adhesion between the hydrophilic fibres and the hydrophobic matrix could be increased. In the electron beam process of the present invention, the fibres are coated with an electron beam-curable monomer/oligomer mixture. This  
25 mixture includes for example unsaturated oligomers, vinyl monomers, acrylated monomers or mixtures thereof. More specifically, the coupling agents of the present invention are preferably epoxy acrylates, polyester-urethane acrylates and polyether acrylates or mixtures  
30 thereof. A specific example of coupling agents includes  
35

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a mixture of hexanediol diacrylate, long-chain acrylated diol, tripropylene glycol diacrylate, vinyl ester resin and isodecyl acrylate.

Chemical bonds are easily produced at both the  
5 matrix/coating interface and the coating/fibre interface,  
using the process of the present invention. The amount  
of bonding is a function of the applied dose, which is  
easily controlled. This chemical bonding improves the  
mechanical properties of thermoplastics containing wood  
10 fibres. In the present invention, the mixture is  
electron beam treated to a dose of 5 to 50 kGy, more  
preferably 6 to 16 kGy.

In addition to the components discussed above  
other product additives such as antioxidants and fibre  
15 dispersion aids can be added, provided that the physical  
properties of the resulting product are not adversely  
affected.

The following examples illustrate the best modes  
contemplated for carrying out this invention, but are not  
20 to be construed as limiting.

Example 1

Wood fibres were coated with 5%, related to the  
fibre mass, of a mixture comprising hexanediol diacrylate  
25 (30%), long chain acrylated diol (20%), tripropylene  
glycol diacrylate (20%), vinyl ester resin (20%) and  
isodecyl acrylate (10%) and a mixture of 25% fibres and  
75% (by weight) polypropylene was prepared. The mixture  
was electron beam treated at a dose of 10 kGy. The  
30 resulting mixture was then further processed by mixing  
using a low shear Henschel blender, extrusion and  
injection moulding.

The resulting material was then subjected to a  
number of tests of the American Society for Testing and  
35 Materials (ASTM) to determine for example, flexural

modulus, flexural strength, tensile modulus, tensile strength, impact strength, and the coefficient of thermal expansion. These tests are standard tests known in the art. The properties of this material (20% WF, 10 kGy) were compared to: unmodified polypropylene material (PP); a commercially available product of polypropylene (Himont PP) and a composite as described above which was not electron beam cured (20% WF, 0 kGy). These results are found in Table 1.

10

Example 2

Thirty-five percent wood fibres were coated with the coupling agents as described in Example 1. The coated fibres were mixed with 63% polypropylene. The mixture was electron beam treated at a dose of 10 kGy. The resulting mixture was then further processed as described in Example 1. The resulting composite material was subjected to the tests referred to in Example 1. The results from these tests are found in Table 1 (35% WF, 10 kGy and 35% WF, 0 kGy).

The last column in Table 1 shows the percent change using 35% wood fibre between the unirradiated and irradiated composite material. It will be readily noted that the flexural modulus, and flexural strength increased in the irradiated composite material as compared to the unirradiated composite material. There was no change in the tensile modulus property between the unirradiated and the irradiated samples. However, the tensile strength and impact strength increased in the materials irradiated as compared to the unirradiated materials. The coefficient of thermal expansion decreased in the irradiated sample.

The results from these tests clearly show that the chemical bonding produced in the present invention improves the mechanical properties of thermoplastics

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containing wood fibres.

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Table 1  
Wood fibre Polypropylene Composite Physical Properties

Property	PP	35% WF				Irradiated vs Unirradiated	
		Himont PP	20% WF 0 kGy	20% WF 10 kGy	35% WF 0 kGy	35% WF 10 kGy	% change
Flexural Modulus, GPa	1.41	1.7	2.17	2.25	3.04	3.46	13.98
Std. Dev.	0.03	0.03	0.08	0.04	0.04	0.03	
Flexural Strength, MPa	37.81	39.11	46.38	44.01	62.47	41.95	
Std. Dev.	0.21	0.12	0.89	0.25	0.79		
Tensile Modulus, GPa	1.87	3.00	2.76	3.93	3.89		
Std. Dev.	0.07	0.16	0.14	0.18	0.10		
Tensile Strength, MPa	37.26	33.11	35.12	35.29	48.80	38.29	
Std. Dev.	0.53	0.88	0.73	1.35	0.78		
Impact Strength, Izod, unnotched, J/m	675.	131.	92.	87.	101.	16.86	
Std. Dev.	28.	8.	7.	11.	11.		
Coefficient of Thermal Expansion, °C <sup>-1</sup> (x10 <sup>6</sup> )	134.3	48.3	45.1	22.4	18.1	-19.20	

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Example 3

Thirty-five percent wood fibres were mixed with  
5 1.75% of a coupling agent consisting of:  
16.6% aliphatic polyester-urethane-acrylate,  
15.0% aromatic polyester-urethane-acrylate,  
1.7% epoxidized soya oil acrylate,  
3.0% poly(propylene glycol) diacrylate,  
10 3.3% neopentyl glycol diacrylate,  
24.0% hexane diol diacrylate, and  
33.4% tri(propylene glycol) diacrylate.  
and mixed with 52% of polypropylene homopolymer, having a  
Melt Flow Index (MFI) of 10g/10 min, and with 13% of and  
15 ethylene-propylene copolymer.  
The dry blend was first mixed in a high-speed fluid  
mixer and then extruded using a twin-screw extruder and  
pelletized. The above described pellets were treated  
with electron from an electron accelerator having a 10  
20 MeV beam energy, to an absorbed dose of 10 kGy. The EB-  
treated pellets were re-pelletized on the same twin-screw  
extruder 76 hours after being irradiated. Table 2 shows  
the main properties, determined as described in Example  
1, of the EB-treated composite made according to the  
25 present invention as compared to the unirradiated mixture  
having the same polymer and fibre composition.

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**Table 2**  
**Properties of Wood Fibre Reinforced Plastics**  
**Modified with Co-Polymers and EB-Treatment**

5

	Property	Composition <sup>1</sup>		
		PP+EP	PP+EP (65%) +WF (35%)	PP+EP (65%) +WF (35%) +EB
10	Flexural Strength, MPa	34.6	32.3	39.6
15	Flexural Modulus, GPa	1.88	3.39	3.75
15	Impact Strength, J/m (Unnotched)	>250	64.7	67.7

20 <sup>1</sup>PP: Polypropylene; EP: Ethylene/propylene copolymer; WF: Wood fibres; EB: Electron beam treatment.

It is understood that the invention has been disclosed herein in connection with certain examples and embodiments. However, such changes, modifications or equivalents as can be used by those skilled in the art are intended to be included. Accordingly, the disclosure is to be construed as exemplary, rather than limiting, and such changes within the principles of the invention as are obvious to one skilled in the art are intended to be included within the scope of the claims.

Claims

1. A process for the production of a thermoplastic composite material containing thermoplastic polymer, cellulosic fibres and coupling agents, comprising the steps of:
  - (a) treating the fibres with EB-curable coupling agents, wherein the coupling agent is selected from the group consisting of unsaturated oligomers, vinyl monomers, acrylated monomers, and mixtures thereof;
  - (b) mixing the treated fibres with thermoplastic polymer material.
  - (c) electron beam treating the mixture to initiate the chemical curing of the coupling agents by producing free radicals; and
  - (d) compounding the EB-treated mixture to form chemical bonds at the fibre-resin interface and the resin-polymer interface.
2. The process of claim 1 wherein 10-50% by weight of the cellulosic fibres are treated with EB-curable coupling agents in an amount of 1 to 10% by weight, relative to the fibres and the treated fibres are mixed with 45 to 90% by weight, of the thermoplastic polymer.
3. The process of Claim 2 wherein the mixture is electron-beam treated to a dose of 5 to 50 kGy.
4. The process of Claim 2 wherein the 20 to 35% by weight, of the cellulosic fibres are treated with EB-curable agents in an amount of 1.5 to 7% by weight, relative to the fibres and the treated fibres are mixed with 55 to 75% by weight, of the thermoplastic polymer.

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5. The process of Claim 4 wherein the mixture is electron-beam treated to a dose of 6 to 16 kGy.

6. The process of Claim 1 wherein the coupling agent is selected from the group consisting of epoxy acrylates, polyester-urethane-acrylates and polyether acrylates or mixtures thereof.

7. The process of Claim 4 wherein the coupling agent is a mixture of hexanediol diacrylate, long chain acrylated diol, tripropylene glycol diacrylate, vinyl ester resin and isodecyl acrylate.

8. The process of Claim 1 wherein the thermoplastic polymer is selected from the group consisting of polypropylene, polyethylene, polyvinylchloride, copolymers of olefines, styrenics, acrylics, polyamides, polyesters and polycarbonates.

9. The process of claim 8 wherein the thermoplastic polymer is selected from the group consisting of polypropylene, polyethylene and polyvinylchloride.

10. The process of Claim 1 wherein the thermoplastic powder has a melt flow index greater than 5 grams per 10 minutes.

11. The process of Claim 1 wherein the compounding, of the cured mixture, is selected from the group consisting of extrusion, injection moulding, calendering and thermoforming.

12. The process of claim 1 wherein the cellulosic fibres are wood fibres.

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13. The process of claim 11 wherein the thermoplastic composite material is electron beam treated after compounding the mixture.

14. The process of claim 1 wherein the production of a thermoplastic composite material containing thermoplastic polymer, wood fibres and EB-curable coupling agents, comprises the steps of:

- (a) treating the wood fibres, 20-35% by weight of the total composite, with EB-curable coupling agents comprising a mixture of hexanediol diacrylate, long chain acrylated diol, tripropylene glycol diacrylate, vinyl ester resin and isodecyl acrylate; in an amount of 1.5 to 7% by weight, relative to the fibres;
- (b) mixing the treated fibres with thermoplastic polymer powder, 55 - 75% by weight of the total composite material;
- (c) electron beam treating the mixture to a dose of 6-16 kGy, to cure the coupling agents and to produce free radicals; and compounding the cured mixture to form chemical bonds at the fibre-resin interface and the resin polymer interface.

## INTERNATIONAL SEARCH REPORT

International Application No PCT/CA 91/00370

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)<sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 08 J 5/06

## II. FIELDS SEARCHED

Minimum Documentation Searched<sup>7</sup>

Classification System	Classification Symbols
IPC5	C 08 J

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in Fields Searched<sup>8</sup>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

Category	Citation of Document <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	US, A, 4464510 (CZVIKOVSKY ET AL) 7 August 1984, see the whole document  --	1-14
A	CA, A, 1269187 (BESHAY, ALPHONS D) 15 May 1990, see the whole document  -----	1-14

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## IV. CERTIFICATION

Date of the Actual Completion of the International Search

14th January 1992

Date of Mailing of this International Search Report

31. 01. 92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

  
Nuria TORIBIO

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.PCT/CA 91/00370

SA 52140

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4464510	07/08/84	DE-A-C- 3230888 GB-A-B- 2104903	03/03/83 16/03/83
CA-A- 1269187	15/05/90	NONE	

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